

Abstract No. song399

**Formation of Mo-containing Nanoparticles on Au(111) from a Mo(CO)<sub>6</sub> Precursor**

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Beamline(s): U7A

**Introduction:** Mo-based catalysts, eg. MoS<sub>2</sub>, Mo<sub>2</sub>C, MoO<sub>3</sub>, are widely used in the petroleum chemical industry. They are active for a range of reactions including olefin metathesis, alkene hydrogenation, isomerization[1] and hydrotreatment of oil-derived feedstock (HDS, HDN, HDO)[2]. MoS<sub>2</sub> is also able to catalyze the synthesis of alcohol from syngas[3]. MoO<sub>3</sub> is active in the selective oxidation of methanol. In this study, we first tried to control the growth of the cluster in nano scale, and then characterize the cluster's properties and reactivity vs. the size of the clusters.

**Methods and Materials:** All the Mo-containing clusters were grown on a Au(111) surface. The source of Mo was Mo(CO)<sub>6</sub>. A S source was used to react with metallic Mo to make MoS<sub>x</sub>. NO<sub>2</sub> was used to oxidize Mo to make MoO<sub>3</sub>. C<sub>2</sub>H<sub>4</sub> was used to react with Mo(CO)<sub>6</sub> on Au(111) to form MoC<sub>x</sub>. Synchrotron-based high resolution photoemission spectroscopy (PES) was used to monitor the growth and characterize the reactivity of these clusters.

**Results:** Mo(CO)<sub>6</sub> is an effective precursor for the preparation of Mo, MoS<sub>x</sub>, MoO<sub>3</sub>, MoC<sub>x</sub> nanoparticles on a Au(111) surface. On this surface the carbonyl adsorbs intact at 100 K and desorbs at temperatures lower than 300 K. Under these conditions, the dissociation of the Mo(CO)<sub>6</sub> molecule is negligible and a desorption channel clearly dominates. An efficient dissociation channel was found after dosing Mo(CO)<sub>6</sub> at high temperatures (>400K). The decomposition of Mo(CO)<sub>6</sub> yields the small coverages of pure Mo that are necessary for the formation of Mo nanoclusters on the Au(111) substrate. At large coverages of Mo (>0.15 ML), the dissociation of Mo(CO)<sub>6</sub> produces also C and O ad-atoms. Mo nanoclusters bonded to Au(111) exhibit a surprising low reactivity towards CO. Mo/Au(111) surface with Mo coverage below 0.1 ML adsorb the CO molecule weakly (desorption temperature < 400 K) and do not induce C-O bond cleavage. The systems of Mo/Au(111), MoS<sub>x</sub>/Au(111), and MoC<sub>x</sub>/Au(111), however, are able to induce the dissociation of thiophene or SO<sub>2</sub>. The formed MoS<sub>x</sub> species are more reactive towards thiophene than extended MoS<sub>2</sub>(0002) surface, MoS<sub>x</sub> films or MoS<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts. This could be a consequence of special adsorption sites and/or distinctive electronic properties that favor bonding interactions with sulfur-containing molecules. MoO<sub>3</sub> particles, formed by reaction of NO<sub>2</sub> with Mo/Au(111) at 500K, are stable below 700K. Above this temperature, MoO<sub>3</sub> desorbs from the surface, and leave a clean Au surface.

**Acknowledgements:** This research was carried out at Brookhaven National Laboratory under contract DE-AC02-98CH10086 with the US Department of Energy (Division of Chemical Sciences). The National synchrotron Light Source is supported by the Materials and Chemical Sciences Divisions of the US Department of Energy.

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